

Role of Bose enhancement in photoassociation*

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Abstract

We discuss the role of Bose enhancement of the dipole matrix element in photoassociation, using stimulated Raman adiabatic passage as an example. In a nondegenerate gas the time scale for coherent optical transients tends to infinity in the thermodynamic limit, whereas Bose enhancement keeps this time scale finite in a condensate. Coherent transients are therefore absent in photoassociation of a thermal nondegenerate gas, but are feasible if the gas is a condensate.

1 Introduction

The theoretical realization is now emerging that it may be possible to effect analogs of coherent optical transients, such as Rabi flopping [1, 2], rapid adiabatic passage [2], and stimulated Raman adiabatic passage (STIRAP) [3], in photoassociation of a Bose-Einstein condensate (BEC). In contrast, the feasibility of transients in PA of a thermal nondegenerate gas has been controversial. There are predictions of STIRAP in ordinary gases [4], whereas our results suggest otherwise [5].

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The purpose of the present paper is to clarify the status of coherent optical transients in both nondegenerate and degenerate thermal gases. Our key concept is Bose enhancement. Suppose we have a large number of atoms N in one quantum state, as in a BEC [6]. Due to Bose-Einstein statistics, the transition matrix element referring to the BEC will pick up a multiplicative factor \sqrt{N} as compared to the matrix element for a single atom. It turns out that Bose enhancement will make a difference. In the thermodynamic limit, when the volume and particle number of a gas tend to infinity while the density remains constant, coherent optical transients will vanish in photoassociation of a nondegenerate gas, but Bose enhancement will facilitate such transients in a condensate. In the rest of the present paper we outline the details of this argument using STIRAP as our explicit example.

2 Ordinary STIRAP

As a prelude to our development we briefly reiterate the salient features of STIRAP in an ordinary three-level Λ system [7], as in Fig. 1. Two laser fields are tuned to exact two-photon resonance between the two lower states a and g of the Λ system. First the laser intensities are arranged in such a way that the coupling between states g and b is much stronger than the coupling between a and b . One of the dressed states of the three-level system then coincides with the bare state a . When the laser intensities are adjusted in such a way that the coupling becomes much stronger in the transition from a to b , the dressed state that initially coincided with the bare state a turns instead into the bare state g .

Suppose now that, before the adjustment of laser intensities, the system started in the bare state a . It then also started in the dressed state whose fate we follow. If the lasers were adjusted slowly enough, adiabaticity guarantees that the system stays in

the dressed state all along. In the end, the system therefore winds up in the bare state g . Moreover, a detailed analysis shows that, in the ideal adiabatic limit, there is never any population at all in the intermediate state b .

In short, the intensities of the two light pulses are switched in such a way that initially the coupling between the unoccupied states is much stronger than the coupling to the occupied state, and the same situation prevails when the coupling strengths have reversed. This is called counter-intuitive pulse order. The result is that the system is transferred from the initial state a to the final state g . Besides, ideally, the system never visits the intermediate state b , which is a major virtue if b is plagued by dissipation.

3 Quasicontinuum photoassociation

In a process of photoassociation two atoms and a photon combine to make the corresponding diatomic molecule. As the two atoms may be considered to be a dissociated state of the molecule, photoassociation is really about free-bound transitions. There are internal atomic and molecular states involved in photoassociation as well, but we assume that, by properly choosing the laser frequency, one has selected a transition from the initial state of the atoms to a unique rovibrational state of the molecule.

Quantum optics normally deals with bound-bound transitions responsible for characteristic spectral lines, and with bound-free transition that manifest themselves in decay processes such as spontaneous emission. From this angle, photoassociation is irreversible decay in reverse, and may seem to violate the second law of thermodynamics. Nonetheless, photoassociation spectroscopy is alive and well, and is the source of the most accurate molecular structure data available at this time [8].

To model free-bound transitions, especially in a thermal sample, it is desirable to start with two atoms whose relative motion is in an eigenstate of energy. Unfortunately,

as energy eigenstates of the relative motion for unconfined atoms are not normalizable, there is no mathematically sound way to write down such a quantum state. The cure is straight from textbooks of quantum mechanics: Assume that the relative motion is restricted to a quantization volume V , and at the end of the calculations take the limit $V \rightarrow \infty$.

This is the stratagem of our quasicontinuum (QC) approach [5, 9]. The dissociation continuum is broken up into discrete states, a QC, whereupon problems with the normalization of the states vanish. In an unexpected windfall, the mathematics also turns out to work out in such a way that the experience about few-level systems gained over decades of quantum optics and laser spectroscopy is directly transferable to understanding photoassociation.

As it comes to the theme of the present paper, the observation of most immediate relevance is that the dipole matrix element between any free (two-atom) state and the bound (rovibrational molecular) state scales with the quantization volume as $d \sim V^{-1/2}$. There is no mystery to this. A unit-normalized dissociated state fills the entire volume V , so its square is proportional to $1/V$ and the normalization constant is $\propto V^{-1/2}$. On the other hand, the normalization constant of the bound state is independent of V . Eventually the $V^{-1/2}$ makes its way to the free-bound dipole matrix element.

The immediate consequence is that in the limit of an infinitely large quantization volume, the dipole matrix element between the bound state and any single QC state vanishes. Accordingly, when the volume is increased and Bose enhancement is absent, the photoassociation coupling can always be treated with perturbation theory [9].

4 Nondegenerate thermal gas

4.1 Theoretical method

The main reason why we have insisted on eigenstates of energy is the basic random-phase postulate of statistical mechanics, which states that the thermal density operator is diagonal in eigenstates of energy. It is therefore always permissible to do whatever analysis one is aiming at by first assuming that the system starts in a given eigenstate of energy m , and at the end of the calculations averaging the results over the thermal probability distribution of the states m .

When discussing a nondegenerate thermal gas, we make another assumption as well. We analyze photoassociation for just two atoms, and calculate the free-bound transition rate, R . However, a typical experiment involves $N \gg 2$ atoms. When thinking of photoassociation of any given ‘probe’ atom, we add the transition rates due to all colliders, so that the photoassociation rate per atom becomes NR .

In the limit of infinite quantization volume, the rate of photoassociation for two atoms vanishes with the coupling matrix element as $R \propto d^2 \propto 1/V$. We of course expect as much since two atoms cease to collide in an infinite volume. Nonetheless, for N atoms the photoassociation rate per atom is $NR \propto N/V = \varrho$, proportional to the density of the gas. In the thermodynamic limit when both N and V tend to infinity in such a way that ϱ remains constant, the photoassociation rate per atom has a finite limit proportional to density. The result is reasonable, and our QC approach [5, 9] in fact exactly reproduces the free-bound transition rate obtained from collision theory [8].

4.2 The demise of STIRAP

In our model, and in current practice [8], the primary photoassociated molecular state is reached by absorption of a photon. This invariably means that the molecule is subject to spontaneous emission, and decays away. Moreover, the reverse of PA, pho-

to dissociation, tends to break molecules back into atoms. It is then a natural idea to add a second laser field tuned between the initially photoassociated state and another (more) stable molecular state, and to attempt to utilize STIRAP to avoid losses from the primary photoassociated state [4]. We sketch such a scheme in Fig. 2.

Unfortunately, this idea hits a roadblock. According to the random-phase postulate, for a thermal sample we may assume that the system starts in a given QC state m , as denoted in Fig. 2. But the free-bound matrix element d scales with the quantization volume V as $d \propto V^{-1/2}$, and tends to zero with $V \rightarrow \infty$. On the contrary, the bound-bound matrix element is volume independent. The free-bound coupling is therefore always small compared to the coupling for bound-bound transitions, and it is impossible to effect the counter-intuitive reversal of the coupling strengths needed for STIRAP [5]. Of course, the final average over a distribution of initial states m is not expected to create STIRAP either.

We are not arguing that there would be no two-color photoassociation; see Ref. [9]. However, in the absence of any evidence to the contrary, we do not believe that the advantages of counter-intuitive pulse order and STIRAP, protection from decay of the intermediate state and the ensuing improvement in transfer efficiency, will materialize in free-bound-bound photoassociation of a thermal nondegenerate gas.

5 Bose-Einstein condensate

5.1 Theoretical method

Calculating the free-bound transition rate for one pair of atoms and then multiplying by the number of available colliders is a process which implicitly assumes that we can distinguish between the atoms. Such an approach is fundamentally flawed in the case of a BEC. Instead, we have adopted a phenomenological second-quantized Hamiltonian

for photoassociation [1, 2].

Our basic premises are that one may treat atoms and molecules as bosons in their own right, and that photoassociation conserves momentum. Given the momentum representation for atoms and molecules, annihilation operators $a_{\mathbf{k}}$ and $b_{\mathbf{k}}$, the part of the Hamiltonian responsible for photoassociation reads,

$$H = \dots - \frac{1}{2} \sum_{\mathbf{k}, \mathbf{p}, \mathbf{q}} \mathbf{d}(\mathbf{k} - \mathbf{p}) \cdot \mathbf{E}_{\mathbf{q}} b_{\mathbf{k} + \mathbf{p} + \mathbf{q}}^{\dagger} a_{\mathbf{k}} a_{\mathbf{p}} + \dots \quad (1)$$

Here $\mathbf{E}_{\mathbf{q}}$ is the Fourier component \mathbf{q}/\hbar of the positive frequency part of the electric field driving photoassociation. By translational symmetry, the dipole matrix element may depend only on the difference of the momenta of the atoms, $\mathbf{k} - \mathbf{p}$, and in the dipole approximation it cannot depend on the photon momentum \mathbf{q} . The term written down is simply a sum of processes in which two atoms with momenta \mathbf{k} , \mathbf{p} and a photon with momentum \mathbf{q} are combined into a molecule with momentum $\mathbf{k} + \mathbf{p} + \mathbf{q}$.

It remains to determine the values of the dipole matrix elements \mathbf{d} in the Hamiltonian. We do this by demanding that for the nondegenerate thermal gas the results from the Hamiltonian (1) be the same as we obtain from our QC approach. In the process a number of subtleties come up having to do, e.g. with Bose-Einstein statistics and the Wigner threshold law for photodissociation [2, 10]. The bottom line, though, is that we know how to deduce the matrix elements from considerations such as the standard molecular-structure calculations, or measurements of the photodissociation rate.

Consider now an ideal zero-momentum condensate photoassociated by a plane wave of light, where all photons have momentum \mathbf{q} . The molecules made by photon absorption all have the momentum \mathbf{q} . The converse is not trivially true. By momentum conservation alone, the induced emission of a molecule with momentum \mathbf{q} need not return two atoms into the condensate; but, in a process we call rogue photodissociation [10], the two atoms may emerge with any opposite nonzero momenta. However, the

photodissociation processes that return the atoms back to the condensate are favored by Bose enhancement, and rogue photodissociation is further suppressed by energy conservation. Thus we adopt a two-mode model, only taking into account atoms with zero momentum and molecules with momentum \mathbf{q} . The corresponding creation and annihilation operators are denoted by a and b .

5.2 The return of STIRAP

Turning now towards two-color photoassociation of a degenerate gas [11], we reconsider the possibility of STIRAP [3]. It is thus assumed that a further laser beam couples the primarily photoassociated molecule to another bound molecular state, whose annihilation operator is denoted by g . The three-mode Hamiltonian reads

$$\frac{H}{\hbar} = -\Delta g^\dagger g - \delta b^\dagger b - \frac{1}{2}\kappa(b^\dagger aa + ba^\dagger a^\dagger) - \frac{1}{2}\Omega(b^\dagger g + bg^\dagger). \quad (2)$$

Here Δ and δ are the two-photon and intermediate detunings, including the proper photon recoil energies, the free-bound QC Rabi frequency is

$$\kappa = \frac{\mathbf{d} \cdot \mathbf{E}}{2\hbar} \quad (3)$$

and Ω is the bound-bound Rabi frequency.

Given the Hamiltonian (2), the Heisenberg equations of motion for the boson operators read

$$\dot{a} = i\kappa a^\dagger b, \quad (4)$$

$$\dot{b} = i\delta b + \frac{1}{2}i(\kappa aa + \Omega g), \quad (5)$$

$$\dot{g} = i\Delta g + \frac{1}{2}i\Omega b. \quad (6)$$

Suppose now that, if all molecules were dissociated to atoms, there were N atoms. The boson operators in the system are then of the order \sqrt{N} . We thus introduce the

rescaled boson operators $\alpha = a/\sqrt{N}$, \dots . These operators are of the order of unity, and may roughly be interpreted as the second-quantized counterparts of the probability amplitudes that an atom is in the atomic condensate (α) or in one of the two molecular condensates (β, γ). The scaled operators obey the equation of motion

$$\dot{\alpha} = i\chi\alpha^\dagger\beta, \quad (7)$$

$$\dot{\beta} = i\delta\beta + \frac{1}{2}i(\chi\alpha\alpha + \Omega\gamma), \quad (8)$$

$$\dot{\gamma} = i\Delta\gamma + \frac{1}{2}i\Omega\beta. \quad (9)$$

The key point of our argument emerges from an inspection of the new Rabi frequency after scaling,

$$\chi = \frac{\sqrt{N}\mathbf{d} \cdot \mathbf{E}}{2\hbar}. \quad (10)$$

The \sqrt{N} is nothing but Bose enhancement in the present context. In the thermodynamic limit $\mathbf{d} \propto \sqrt{1/V}$, so that $\chi \propto \sqrt{N/V} = \sqrt{\rho}$ remains finite. More precisely, suppose that the same laser field with amplitude \mathbf{E} were tuned in such a way that the the photodissociation of bound molecules would produce two atoms with the reduced mass μ and relative velocity v at the rate $\Gamma(v)$, then we have [2, 10]

$$\chi = \lim_{v \rightarrow 0} \sqrt{\frac{2\pi\hbar^2\Gamma(v)\varrho}{\mu^2v}}. \quad (11)$$

The limit is finite and nonzero by virtue of the Wigner threshold law.

The couplings χ and Ω in Eqs. (7)-(9) do not depend on the quantization volume anymore; the dependence on V is replaced by a dependence on ϱ , the density of atoms if all molecules were to dissociate. In a BEC there is no longer any intrinsic restriction on the relative size of the couplings, and photoassociative STIRAP is feasible even in the thermodynamic limit.

We have constructed explicit examples of STIRAP by solving Eqs. (7)-(9) in a semi-classical or mean-field [6] approximation, treating α, β and γ as *c*-numbers instead of

quantum operators [3]. Unlike the equations for probability amplitudes for the ordinary Λ system, these equations are nonlinear. Nonetheless, the basic character of STIRAP remains intact. In particular, for completely adiabatic switching of pulse strengths (for which Ref. [3] gives quantitative criteria), there is never any probability in the primary photoassociated state. Spontaneous-emission losses and rogue photodissociation are then shut off.

We cannot think of any matter of principle that could go catastrophically wrong with STIRAP. In practical experiments the atoms and possibly also the molecules are trapped and do not form infinite homogeneous condensates. Trapped particles come with a time scale that is of the order of tens of milliseconds in the magnetic case. If the STIRAP pulses are faster, trapping should not matter a whole lot. We have also ignored collisions between atoms, between molecules, and between atoms and molecules. But again, the corresponding time scales could easily be much longer than the time scale of the laser pulses, so that collisions are also negligible. The worst practical enemy of STIRAP might be light shifts of the two-photon resonance, which come about as a result of virtual transitions accompanying rogue photodissociation [9, 10]. However, in principle one can always compensate for light shifts by chirping the laser pulses.

6 Ruminations

Our renunciation of photoassociative STIRAP in a thermal nondegenerate gas most likely applies to other coherent optical transients as well [9]. In the limit $V \rightarrow \infty$ the free-bound Rabi frequency $\kappa \propto 1/\sqrt{V}$ tends to zero, and the corresponding time scale for the transient $1/\kappa$ tends to infinity. At least in a large enough sample, something else is likely to happen before a coherent transient can run its course.

Similarly, coherent transients should work in photoassociation of a BEC. Because

of Bose enhancement, the coupling matrix element picks up a the factor \sqrt{N} , giving the effective Rabi frequency $\chi = \sqrt{N}\kappa \propto \sqrt{N/V} = \sqrt{\varrho}$. In the thermodynamic limit χ remains finite, and the time scale of transients actually scales with atom density as $\rho^{-1/2}$. Such transients have already been discussed in the photoassociation literature [1, 2], and equivalent mathematics is involved in a wide variety of topics ranging from second-harmonic generation [12] to the Feshbach resonance [13].

One final point concludes our discussion of transients in photoassociation. Bose enhancement oftentimes makes little practical difference even when it is formally present. For instance, suppose that we were to calculate a transition rate for a condensate under a normal bilinear coupling of the form $b^\dagger a$. Bose enhancement gives the factor \sqrt{N} in the matrix element, and the transition rate for the condensate in terms of the one-atom rate R reads NR . However, in the second quantized formulation all N condensate atoms are treated at once, so that the transition rate per atom is still R . On the other hand, the coupling for photoassociation, $b^\dagger aa$, is trilinear. The ensuing Bose enhancement $\propto (\sqrt{N})^2$ is thus stronger than for a bilinear coupling; in fact, just strong enough to offset the decrease of the coupling matrix element in the thermodynamic limit. As a result of the confluence of BEC and cubic coupling, a condensate responds to photoassociation as a unit on a time scale that depends on density, but oddly enough not directly on atom number or size of the condensate.

7 Acknowledgements

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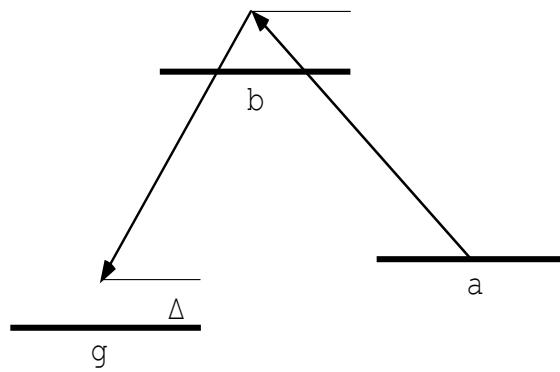


Figure 1: Three-level Λ scheme with states a , b and g and laser couplings with Rabi frequencies κ and Ω . The definitions of the two-photon and intermediate detunings Δ and δ are also given schematically. For STIRAP, one would have $\Delta = 0$. The notation also applies to the Hamiltonian (1).

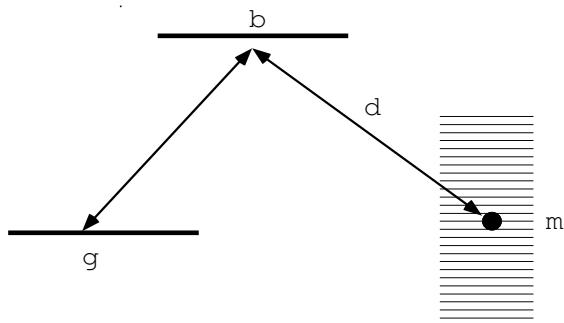


Figure 2: Scheme for STIRAP starting from the quasicontinuum state m . The free-bound coupling is represented here by the dipole matrix element, d .